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Copoly(1,3,4-oxadiazole-ether)s containing phthalide groups and thin films made therefrom

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Abstract

A series of aromatic copolyethers containing 1,3,4-oxadiazole rings and phthalide groups was prepared by nucleophilic substitution polymerization technique of phenolphthalein, **1**, or of an equimolecular amount of **1** and different bisphenols **2**, such as: 4,4′-isopropylidenediphenol, 4,4′-(hexafluoroisopropylidene)diphenol, 4,4′-(1,4-phenylene-diisopropylidene)bisphenol, 4,4′-cyclohexylidene-bisphenol and 2,7-dihydroxynaphthalene, with 2,5-bis(*p*-fluorophenyl)-1,3,4-oxadiazole, **3**. The polymers were easily soluble in polar solvents such as *N*-methylpyrrolidone, *N*,*N*-dimethylacetamide, *N*,*N*-dimethylformamide and chloroform and can be cast from solutions into thin flexible films. They showed high thermal stability, with decomposition temperature being above 400 °C. The polymers exhibited a glass transition temperature in the range of 220–271 °C, with reasonable interval between glass transition and decomposition temperature. Electrical insulating properties of some polymer films were evaluated on the basis of dielectric constant and dielectric loss and their variation with frequency and temperature. The values of the dielectric constant at 10 kHz and 20 °C were in the range of 2.98–3.15.

Keywords: Poly(1,3,4-oxadiazole-ether)s; Thin films; Dielectric spectroscopy

1. Introduction

Aromatic polyethers are well recognized as a class of high-performance engineering thermoplastics with the characteristics of good thermooxidative stability, high glass transition temperature and excellent mechanical strength. One method in the development of these polymers is the incorporation of heterocyclic units into their macromolecular structure [1–6].

The introduction of 1,3,4-oxadiazole rings into the macromolecular chains of aromatic polyethers improves their properties [7–12]. The oxadiazole cycle is similar to a *p*-phenylene structure, which is known to be highly thermoresistant. Also, it does not contain any hydrogen atoms, nor any possibilities of rearrangement, it lacks tension, it has structural symmetry, and it is thermally unreactive [13]. More recently specific properties determined by the electronic structure of oxadiazole ring, especially its electron-withdrawing character, revigourated an intensive research aiming to use such polymers as advanced materials in microelectronics, optoelectronics and others [14,15]. Different methods for the synthesis of poly(1,3,4-oxadiazole-aryl-ether)s are reported in the literature. Some procedures involve polycondensation of a dicarboxylic acid or a diacid chloride with hydrazide sulfate or dihydrazide followed by cyclodehydration of the intermediate polyhydrazide [16,17]. However, the cyclization to oxadiazole ring may be not complete, side reactions and some crosslinking may occur. The method frequently utilized for their preparation is the aromatic nucleophilic substitution polymerization, in which an aromatic bisfluoride activated by strongly electron-attracting 1,3,4-oxadiazole ring is chosen as partner of bisphenols. Polymerization follows a conventional nucleophilic aromatic substitution mechanism via a Meisenheimer complex intermediate,

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the formation of which is the rate-determining step in the polymerization process [18,19].

It has been reported that the solubility of the polymers can be enhanced and they can possess outstanding thermal characteristics by having cyclic side groups such as fluorene, phthalide, phthalimidine groups on the polymer backbone [20–22]. Thus, the introduction of phthalide groups into the macromolecular chains of poly(ether-imide)s improves the properties of the resulting materials. They exhibit high thermal stability, high glass transition temperature and excellent mechanical toughness. In addition, the polymers are soluble in different organic solvents like *N*-methylpyrrolidone (NMP), *N*,*N*-dimethylacetamide, *N*,*N*-dimethylformamide or chloroform and can be cast into flexible tough films. The presence of phthalide groups also improves the optical properties leading to light-colored and fairly transparent polymers [22]. Also, phenolphthalein-based poly(aryl-ether-ketone)s exhibited excellent mechanical and thermal properties. The polymers were easily soluble in different organic solvents and can be cast into flexible tough films. The experimental results on its gas permeability studies revealed that, on comparison with the polymers without phthalide groups, phenolphthalein-based poly(aryl-ether-ketone)s possessed better gas transport properties [23].

An useful approach for reducing the melting temperature of the polymers and increasing the solubility is the copolymerization of monomers by which the symmetry of the structure is lowered and the lateral packing is disrupted. In addition, the introduction of flexible spacers between rigid-rod groups also can be used to lower melting temperature and to improve the solubility [24].

Here is presented the synthesis and characterization of aromatic poly(1,3,4-oxadiazole-ether)s containing phthalide groups. The polymers were prepared by the reaction of phenolphthalein or of an equimolecular amount of the latter and different bisphenols with 2,5-bis(*p*-fluorophenyl)-1,3,4-oxadiazole. The properties of these polymers such as solubility, inherent viscosity, thermal stability, glass transition temperature and electrical characteristics of the films made from these compounds have been evaluated with respect to their chemical structure.

2. Experimental

2.1. Synthesis of the monomers

2,5-Bis(*p*-fluorophenyl)-1,3,4-oxadiazole, **3**, was prepared by the reaction of 4-fluorobenzoic acid with hydrazine hydrate, in polyphosphoric acid [25], m.p.: 200–202 °C.

2.2. Synthesis of the polymers

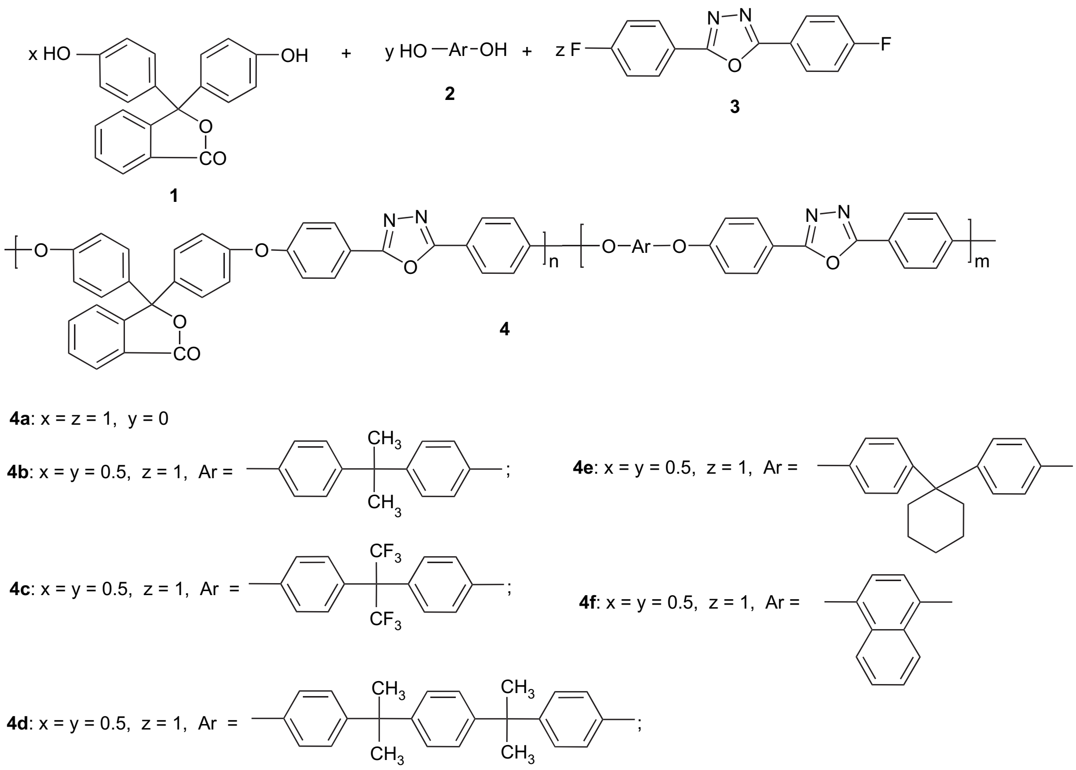
A typical synthesis of poly(1,3,4-oxadiazole-ether) **4a** was conducted in a three-neck flask equipped with a nitrogen inlet, mechanical stirrer, Dean–Stark trap and condenser. The flask was charged with phenolphthalein (0.636 g, 0.002 mol), 2,5-bis(*p*-fluorophenyl)-1,3,4-oxadiazole (0.516 g, 0.002 mol), NMP (5 mL) and toluene (2 mL). An excess of potassium carbonate (0.604 g) was added. The reaction mixture was heated to reflux and water was removed by azeotropic distillation with toluene for 4–6 h. Then the reaction mixture was heated at 170–180 °C for approximately 20 h. After cooling to room temperature, the viscous polymerization mixture was diluted with NMP (10 mL) and it was added dropwise into water. The fibrous polymer was isolated, washed with water, refluxed with methanol, filtered and vacuum dried. For the synthesis of copolyethers **4b–f**, the same method was used, equimolecular amounts of bisphenols **1** and **2** being added (Scheme 1).

2.3. Preparation of polymer films

Films of aromatic copolyethers **4** were prepared by casting a solution of 5% concentration of polymer in chloroform onto glass plates, followed by drying at room temperature for 24 h, under a Petri dish, and for another 2 h at 130 °C [26]. The resulting flexible transparent films were stripped off the plates by immersion in hot water for 2 h.

2.4. Measurements

Melting points of the monomers and intermediates were measured on a Melt-Temp II (laboratory devices). The inherent viscosities (η_{inh}) of the polymers were determined with an Ubbelohde viscometer, by using polymer solutions in NMP, at 20 °C, at a concentration of 0.5 g/dL. Infrared spectra were recorded with a Specord M80 spectrometer by using KBr pellets. ^{1}H NMR spectra were recorded on a Bruker Avance DRX 400 instrument, by using solutions in deuterated chloroform. The molecular weight distributions were measured by gel permeation chromatography with a PL-EMD 950 evaporative mass detector instrument. Polystyrene standards of known molecular weight were used for calibration. Thermogravimetric analysis (TGA) was performed on a MOM derivatograph (Hungary) in air, at a heating rate of 10 °C/min. The initial decomposition temperature (IDT) is characterized as the temperature at which the sample achieves a 5% weight loss. The temperature of 10% weight loss (T_{10}) was also recorded. The glass transition temperature (T_g) of the precipitated polymers was determined with a Mettler differential scanning calorimeter DSC 12E, at a heating rate of 10 °C/min, under nitrogen. Heat flow versus temperature scans from the second heating run were plotted and used for reporting the glass transition temperature. The mid-point of the inflexion curve resulting from the typical second heating was assigned as the glass transition temperature of the respective polymers. The dynamic mechanical analysis (DMA) was conducted using a Perkin–Elmer Diamond apparatus provided with a standard tension attachment at a frequency of 1 Hz. The apparatus was heated between 100 °C and 350 °C at 2 °C/min, in a nitrogen atmosphere. The films (20 × 10 × 0.05 mm) were longitudinally deformed by small sinusoidal stress and the resulting strain was measured. The value of storage modulus E', the loss modulus E'' and tension loss tangent ($\tan \delta = E''/E'$) were obtained as a function of temperature. The mechanical properties of the polymer films were determined by stress–strain measurements of films at room temperature on a TIRAtest 2161 apparatus,



Scheme 1. Synthesis of copoly(1,3,4-oxadiazole-ether)s containing phthalide groups **4**.

Germany. The tests were done with a crosshead speed of 1 mm/min and distance between grips of 43.4 mm. The dielectric measurements were carried out using a Novocontrol system composed from an Alpha frequency response analyzer and Quattro temperature controller. The samples were prepared in the form of films with thickness of about 30 μm with gold electrodes evaporated in vacuum. The samples were sandwiched between two copper electrodes of diameter 20 mm and placed inside temperature controlled sample cell. The complex permittivity: $\varepsilon^*(f) = \varepsilon'(f) + i\varepsilon''(f)$ has been determined in the frequency (f) range from 10^{-1} Hz to 10^{6} Hz and at temperature range from −100 °C to 200 °C. The AC voltage applied to the capacitor was equal to 1.5 V. Temperature was controlled using a nitrogen gas cryostat and the temperature stability of the sample was better than 0.1 °C. The points used for the activation maps were determined from positions of the maxima of the $\varepsilon''(f)$ curves using WinFIT software. The relaxation times (τ) were calculated from the equation: $\tau = 1/(2\pi f_{\max})$, where $f_{\max}$ is the frequency of the relaxation peak at a given temperature T.

3. Results and discussion

3.1. Synthesis procedure

Copolyethers **4** were prepared by the reaction of 2,5-bis-(p-fluorophenyl)-1,3,4-oxadiazole, **3**, with phenolphthalein or with an equimolar amount of phenolphthalein and different bisphenols **2**, such as: 4,4′-isopropylidenediphenol, **2a**, 4,4′-(hexafluoroisopropylidene)diphenol, **2b**, 4,4′-(1,4-phenylene-diisopropylidene)bisphenol, **2c**, 4,4′-cyclohexylidene-bisphenol, **2d**, 2,7-dihydroxynaphthalene, **2e**, as shown in Scheme 1. The polycondensations were carried out at elevated temperature in NMP, in the presence of anhydrous potassium carbonate. The nucleophilic aromatic substitution of an aryl halide with a phenoxide is the most common route to obtain high-performance, high temperature aromatic polyethers.

3.2. Chemical structure and general characterization

The structure of copolymers **4** was identified by IR and NMR spectroscopy. In IR spectra of all polymers characteristic absorption bands appeared at 1240 cm^{-1} due to the presence of aromatic ether linkages and at 1750 cm^{-1} due to the carbonyl of phthalide groups. The absorption bands appearing at 1020 cm^{-1} and 960 cm^{-1} were characteristic of =C–O–C= stretching in 1,3,4-oxadiazole rings. Characteristic bands at 3060 cm^{-1} and 1600 cm^{-1} were due to aromatic C–H stretching and aromatic C–C stretching, respectively. The IR spectra of copolymers **4b** and **4d** revealed characteristic absorption bands of isopropylidene groups at 2980 cm^{-1} and 2880 cm^{-1}. The IR spectrum of polymer **4e** showed absorption bands at 2920 cm^{-1} and 2850 cm^{-1} due to the presence of CH_2 groups. In the case of polymer **4c**, absorption bands of hexafluoroisopropylidene (6F) groups appeared at 1180 cm^{-1} and 1210 cm^{-1}.

Fig. 1 illustrates the ^{1}H NMR spectrum of polymer **4a** with the assignments of all the protons. The protons H_h closer to electron-withdrawing 1,3,4-oxadiazole ring appeared at the farthest downfield region of the spectrum. The protons H_a and H_g shifted to higher field due to the electron donating

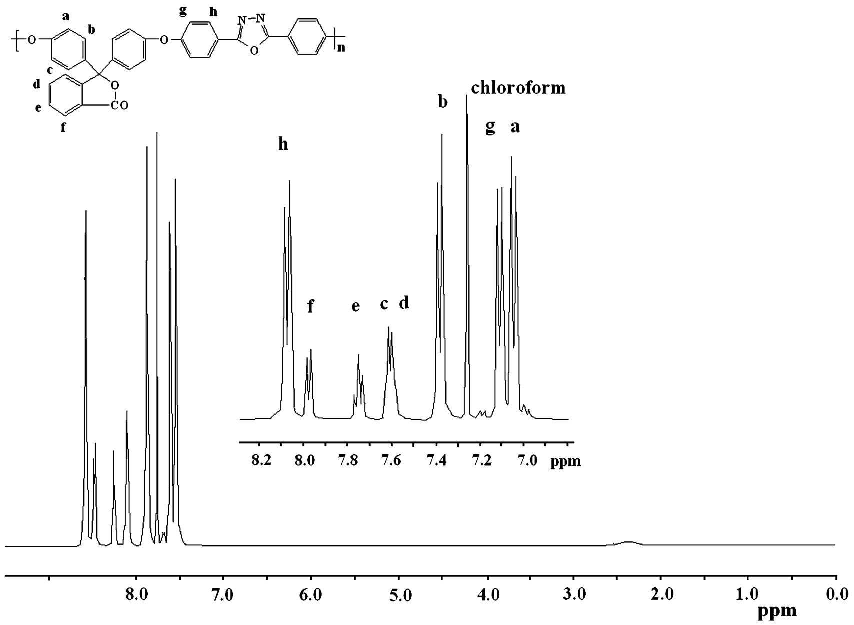


Fig. 1. ^{1}H NMR spectrum of polymer **4a**.

properties of aromatic ether linkages. Fig. 2 shows the ^{13}C NMR spectrum of polymer **4a**. The carbon atoms of 1,3,4-oxadiazole rings C_5 appeared at high ppm value (156 ppm). The carbon atom of carbonyl group of phthalide units C_{17} appeared at the highest ppm value (169.4 ppm). Fig. 3 presents the ^{1}H NMR spectrum of copolymer **4b**, derived from 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole and equimolar amounts of phenolphthalein and 4,4′-isopropylidenediphenol. The aromatic protons coming from the bisphenol segments, H_m and H_n appeared as doublets at 7.00 ppm and 7.05 ppm, respectively. Aliphatic protons of isopropylidene groups H_k appeared at higher values of the field. From the ^{1}H NMR spectra of the copolymers it was found that the composition of the polymer is similar to the composition of the reactants used for the synthesis.

The polymers were soluble in polar solvents like NMP and *N*,*N*-dimethylacetamide and in less polar solvents like pyridine, chloroform or tetrahydrofuran. Except polymer **4c** containing 6F groups all the other polymers were insoluble in *N*,*N*-dimethylformamide (Table 1). The good solubility of the polymers can be explained by the presence of phthalide groups which can disorder the chains and hinder dense chain

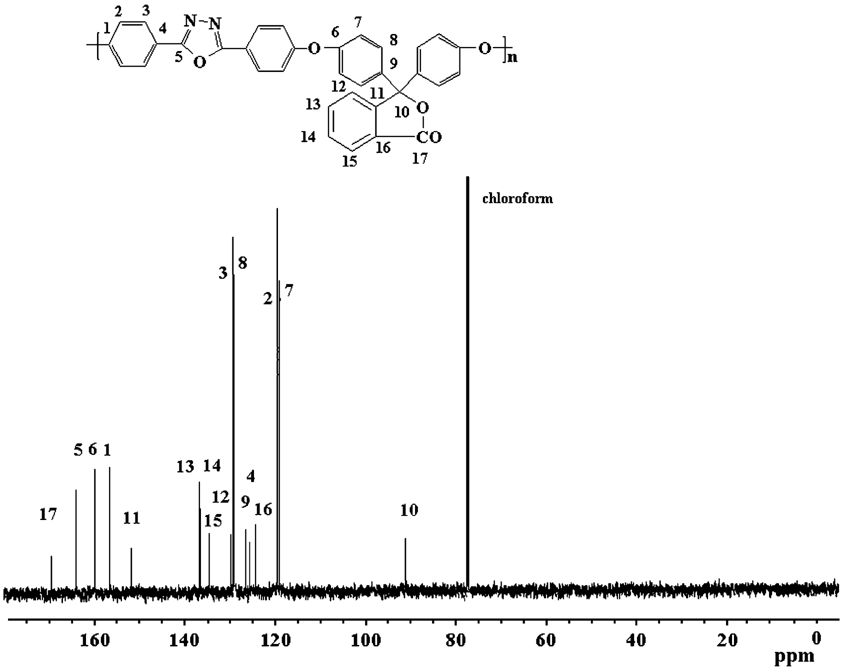


Fig. 2. ^{13}C NMR spectrum of polymer **4a**.

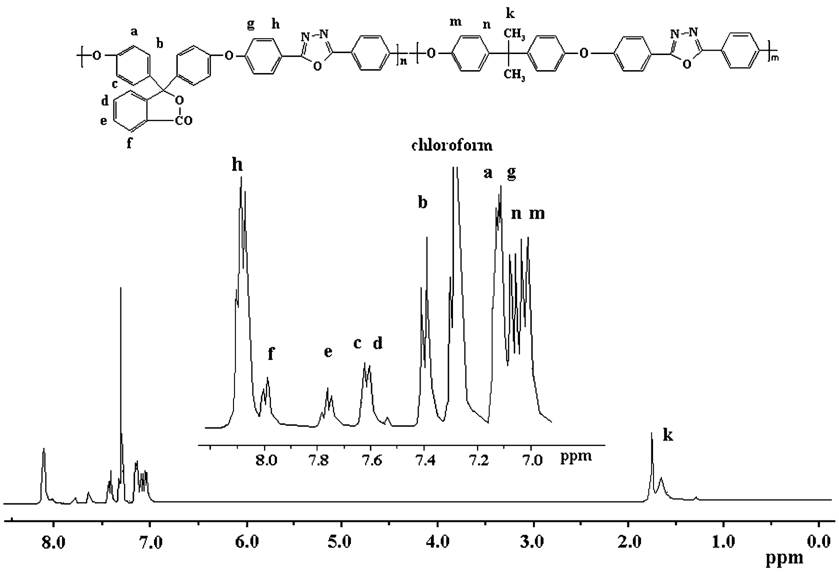


Fig. 3. ^{1}H NMR spectrum of polymer **4b**.

Table 1
Solubility of polymers **4**

Polymer	NMP	DMAc	DMF	Py	$CHCl_3$	DCE	THF	Acetone	CCl_4
4a	+	+	−	+	+	−	+	−	−
4b	+	+	−	+	+	+	+	−	−
4c	+	+	+	+	+	+	+	−	−
4d	+	+	−	+	+	+	+	−	−
4e	+	+	−+	+	+	−+	+	−	−
4f	+	+	−	+	+	−	+	−	−

NMP = *N*-methylpyrrolidone; DMAc = *N*,*N*-dimethylacetamide; DMF = *N*,*N*-dimethylformamide; Py = pyridine; DCE = dichloroethane; THF = tetrahydrofuran; + = soluble; −+ = partially soluble; − = insoluble.

stacking, thereby reducing the interchain interactions lowering the density of cohesive energy and thus improving solubility. The higher solubility of polymer **3c** in *N*,*N*-dimethylformamide was due to the presence in the structure of 6F groups which produced sterical hindrance and did not allow a strong packing of the macromolecular chains; thus the molecules of solvents can penetrate easily through macromolecular chains improving the solubility.

The inherent viscosity of polymers **4** was in the range of 0.58–0.73 dL/g (Table 2). The molecular weight of polymers **4** was determined by gel permeation chromatography (GPC). The values of weight-average molecular weight (M_w) and number-average molecular weight (M_n) were in the range of 40 200–123 000 g/mol and 17 800–68 800 g/mol, respectively. The polydispersity M_w/M_n was in the range of 1.73–2.51 (Table 2). The GPC curves showed narrow molecular weight distribution and low quantity of oligomers.

Table 2
Inherent viscosity and GPC analyses of polymers **4**

Polymer	η_{inh}[a] (dL/g)	M_n (g/mol)	M_w (g/mol)	M_w/M_n
4a	0.73	40 450	70 100	1.73
4b	0.61	37 600	81 500	2.16
4c	0.97	44 600	112 000	2.51
4d	0.58	68 800	123 000	1.78
4e	0.36	17 800	40 200	2.25
4f	0.38	21 000	42 500	2.02

[a] Measured at a concentration of 0.5 g polymer in 100 mL of NMP, at 20 °C.

3.3. Mechanical and thermal properties

Flexible free-standing films were prepared by casting the chloroform solutions of polymers **4a–d**. These films were subjected to tensile tests, and the results are summarized in Table 3. They had a tensile strength of 80–117 MPa, an elongation to break of 2.04–5.49, and an initial modulus of 1.05–2.70 GPa. These data show that the present polymers have tough mechanical properties, comparable to that of related poly(1,3,4-oxadiazole-ether)s not containing phthalide groups [27]. The films of polymers **4e** and **4f** were brittle.

The thermal stability of these polymers was studied by thermogravimetric analysis (TGA). All polymers exhibited high thermal stability. They began to decompose in the range of 405–462 °C, as indicated by the temperature of 5% weight loss in TGA thermograms (Table 4). The temperature of 10% weight loss was in the range of 425–480 °C and the total weight loss at 500 °C was in the range of 30.5–34%. The degradation process exhibited two maxima of decomposition. The first (T_{max1}) was in the range of 430–480 °C and the second maximum of decomposition (T_{max2}) was in the range of 565–630 °C. Polymer **4a**, derived from phenolphthalein, exhibited the highest initial decomposition temperature

Table 3
Mechanical properties of polymer films **4a–d**

Polymer	Tensile strength (MPa)	Modulus (GPa)	Elongation at break (%)
4a	103.0	2.10	3.03
4b	80.2	1.55	5.26
4c	117.5	2.70	2.04
4d	81.2	1.05	5.49

Table 4
The thermal properties of polymers **4**

Polymer	T_g[a] (°C)	T_g[b] (°C)	tan δ[c]	IDT[d] (°C)	T_{10}[e] (°C)	T_{max1}[f] (°C)	T_{max2}[g] (°C)	Weight loss at 500 °C (%)
4a	271	251	1.802	462	470	460	570	34.0
4b	235	232	1.804	405	430	440	565	34.0
4c	240	238	1.850	440	460	480	630	30.5
4d	220	212	1.950	425	450	450	560	36.4
4e	232	–	–	405	425	470	540	36.7
4f	241	–	–	415	440	430	610	33.2

[a] Glass transition temperature, determined from DSC curves.
[b] Glass transition temperature, determined from DMA curves.
[c] Measured at T_g value.
[d] Initial decomposition temperature = the temperature of 5% weight loss.
[e] Temperature of 10% weight loss.
[f] First maximum polymer decomposition temperature.
[g] Second maximum polymer decomposition temperature.

(IDT = 462 °C); the presence of the isopropylidene groups, in the case of polymers **4b** and **4d**, reduced the thermal stability (IDT = 405 °C and 425 °C, respectively). Due to the higher thermal resistance of 6F groups, polymer **4c** exhibited higher initial decomposition temperature (440 °C) when compared with polymers having isopropylidene groups **4b** and **4d**. Also, polymer **4e** showed lower thermal stability (IDT = 405 °C) due to the presence of cyclohexylidene groups more sensible to thermal degradation.

The glass transition temperature (T_g) of the present polymers, evaluated from DSC curves, was in the range of 220–271 °C (Table 4). The DSC measurements showed no evidence of crystallization or melting which proves an amorphous morphology (Fig. 4). T_g is known to depend on the rigidity of the polymer main chain, the increase of the rigidity of the polymer backbone increases the energy barrier and hence T_g increases. Thus, polymer **4a**, containing the highest concentration of bulky phthalide cardo groups, exhibited the highest T_g (271 °C). This polymer exhibited at the same time good solubility and high T_g. This indicates that the decrease in interchain attractions brought about by bulky phthalide groups is well overcome by the effect of skeletal rigidity imparted by phthalide units. It can be seen that by the introduction of the second bisphenol co-monomer a decrease of T_g appeared. As expected, polymer **4c** containing 6F groups exhibited higher T_g (240 °C) when compared with polymers **4b** and **4d** having isopropylidene groups (whose T_g were 235 °C and 220 °C, respectively). For polymers **4** it can be noticed that there is a large interval between the glass transition and decomposition temperature which makes these polymers attractive for thermoforming processing.

By comparing the solubility and T_g of the present polymers with related poly(1,3,4-oxadiazole-ether)s which do not contain phthalide groups [9], it can be seen that the former exhibits higher solubility and T_g values. This fact is probably due to the presence of bulky phthalide groups which disturb the intra- and inter-molecular interactions and decrease the flexibility of the polymer chains. The highest quality of these polymers is their remarkable solubility in organic solvents such as NMP, chloroform, tetrahydrofuran, which associated with their high thermal stability is very important from practical point of view.

Figs. 5 and 6 present the dynamic storage modulus E', and the tangent loss tan δ versus temperature for polymers **4a–d**, respectively. The drops in E' curves and peaks tan δ plots report on the physical transitions in the polymer film. All samples exhibited a relatively narrow α-relaxation peak which corresponds to the glass transition and reflects the onset of large scale chain motions. The T_g values determined by DMA measurements were slightly lower when compared with those determined by DSC measurements (Table 4). The magnitude of the tan δ at T_g is a measure of the energy-damping characteristic of a material and is related with the impact strength of a material. The impact strength increases with the addition of tan δ value at T_g [28]. The tan δ values at T_g are collected in Table 4. The results indicated that the energy-damping characteristics and mechanical properties of

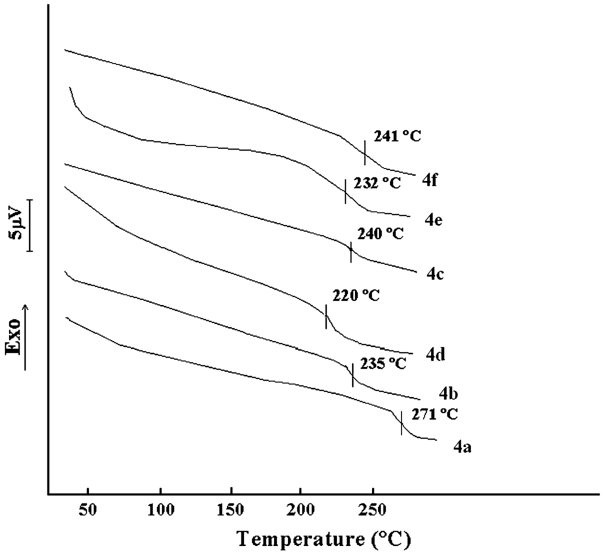


Fig. 4. DSC curves of polymers **4**.

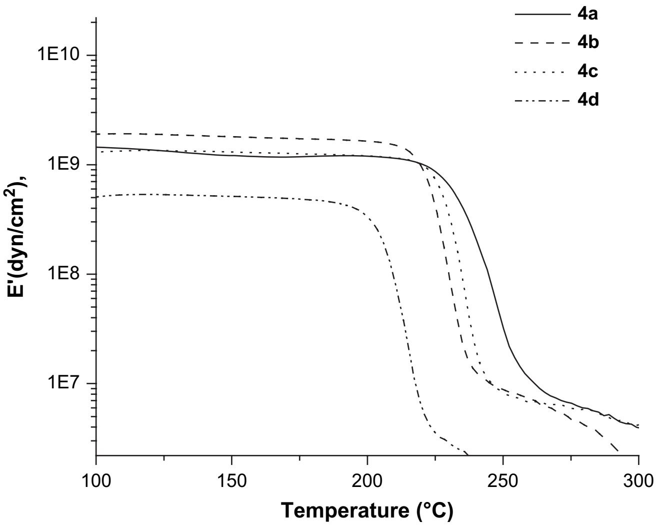


Fig. 5. Temperature dependence of the storage modulus for polymers **4a–d**.

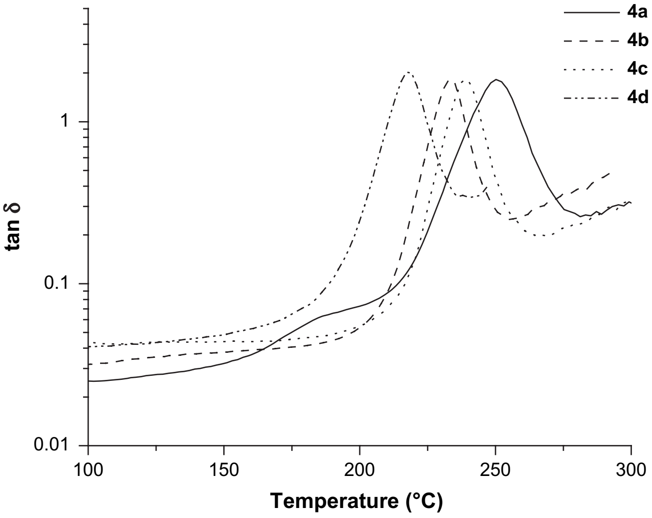


Fig. 6. Temperature dependence of tan δ for polymers **4a**–**d**.

the polymers were similar. Polymer **4d**, containing two isopropylidene groups per unit structure, exhibited slightly higher tan δ value at T_g suggesting superior impact strength of the material.

3.4. Dielectric properties

Electrical insulating properties of polymer films **4a**–**c** were evaluated on the basis of dielectric constant and dielectric loss and their variation with frequency and temperature. The dielectric permittivity of a material is, in general, a complex quantity, when measured in the frequency domain. Its real part (ε') is called the "dielectric constant" and decreases with increasing frequency with characteristic steps. Its imaginary part (ε'') is usually called the "dielectric loss" and may show the maxima on the diagrams vs. frequency (or vs. temperature). Fig. 7 presents the dependence of real and imaginary parts of complex permittivity on frequency, for polymers **4a**–**c**, at three chosen temperatures. From Fig. 7 it can be seen that ε' slightly decreases with increasing frequency when temperature is constant. The dielectric constant of polymers decreased gradually with increasing frequency because the response of the electronic, atomic and dipolar polarizable units vary with frequency. This behavior can be attributed to the frequency dependence of the polarization mechanism. The magnitude of the dielectric constant is dependent upon the ability of the polarizable units to orient fast enough to keep up with the oscillation of the alternative electric field [29]. An increase of the dielectric constant can be observed for polymers **4a** and **4b**, especially at high temperature (180 °C) and low frequency due to the mobility of charge carrier. Polymer **4c**, containing 6F atoms, exhibited low dielectric constant over the entire interval of frequency (10^{-1}–10^{6} Hz) even at 180 °C. For many applications, dielectric materials with stable dielectric constant and dissipation factor values across large frequency and temperature range are highly preferred.

The dielectric constants of polymers **4a**–**c** at 1 Hz, 100 Hz, 10 kHz, and 1 MHz, at room temperature, are presented in Table 5. The values of the dielectric constant at 10 kHz were in the range of 2.98–3.15. As it can be seen from Table 5 these polymers exhibited lower dielectric constant values in comparison with H-Film, a polyimide which is prepared from pyromellitic dianhydride and 4,4′-diaminodiphenylether and which is one of the most common polyimides used as dielectric in microelectronics applications, having a dielectric constant of 3.5 [30].

Although polymers **4** contain polar groups, the bulky phthalide groups increase the free volume of the polymers lowering the polarization by decreasing the number of polarizable groups per unit volume and thus decreasing the dielectric constant. By introduction of isopropylidene groups, in the case of polymer **4b**, a slight decrease of the dielectric constant appeared. Polymer **4c**, containing 6F atoms exhibited the lowest dielectric constant. The 6F atoms could improve the dielectric performance because of the less efficient chain packing and increased free volume. In addition, the strong electronegativity of fluorine atoms results in very low polarizability of the C–F bonds, thus decreasing the dielectric constant [31,32].

At high temperatures the dielectric loss increased sharply with decreasing frequency due to the mobility of charge carrier [33]. Polymers **4a** and **4b** exhibited higher dielectric loss at high temperature and low frequency when compared with that of polymer **4c**, in the same conditions. This may be explained by the presence of a higher concentration of dipoles in the case of polymers **4a** and **4b**, when compared with polymer **4c**. At moderate temperature the dielectric loss exhibited low values in the interval of measured frequency. Low values of the dielectric loss are indicative of minimal conversion of electrical energy to heat in the dielectric material. It is advantageous to have low values for both dielectric constant and dielectric loss because electrical signals loss will be less of their intensity in the dielectric medium.

At 180 °C and low frequency an increase of the ε' and a sharp increase of ε'' especially for polymers **4a** and **4b** can be observed. The strong low-frequency dispersion for ε' and sharp increase of ε'' are the characteristics of charge carrier systems. The localized charge carriers under an applied alternating electric field can hop to neighboring localized sites like the reciprocating motion of a jumping dipole or can jump to neighboring sites, which form a continuous connected network allowing the charges to travel through the entire physical dimensions of the polymer sample and causing the electric conduction. During the motion of charge carriers, the applied electric field will be a subject of decay. Such relaxation of electric field is termed electric field relaxation and the relaxation of the charge system is termed conductivity relaxation [34].

The dielectric loss for polymer film **4a** at different temperatures taken in the range from −100 °C to 180 °C is shown in Fig. 8. There two secondary β and γ relaxation processes, connected with local movements of polymer chain appear. Similar results were also obtained for polymers **4b** and **4c**. The activation map is the best way for a comparison of all

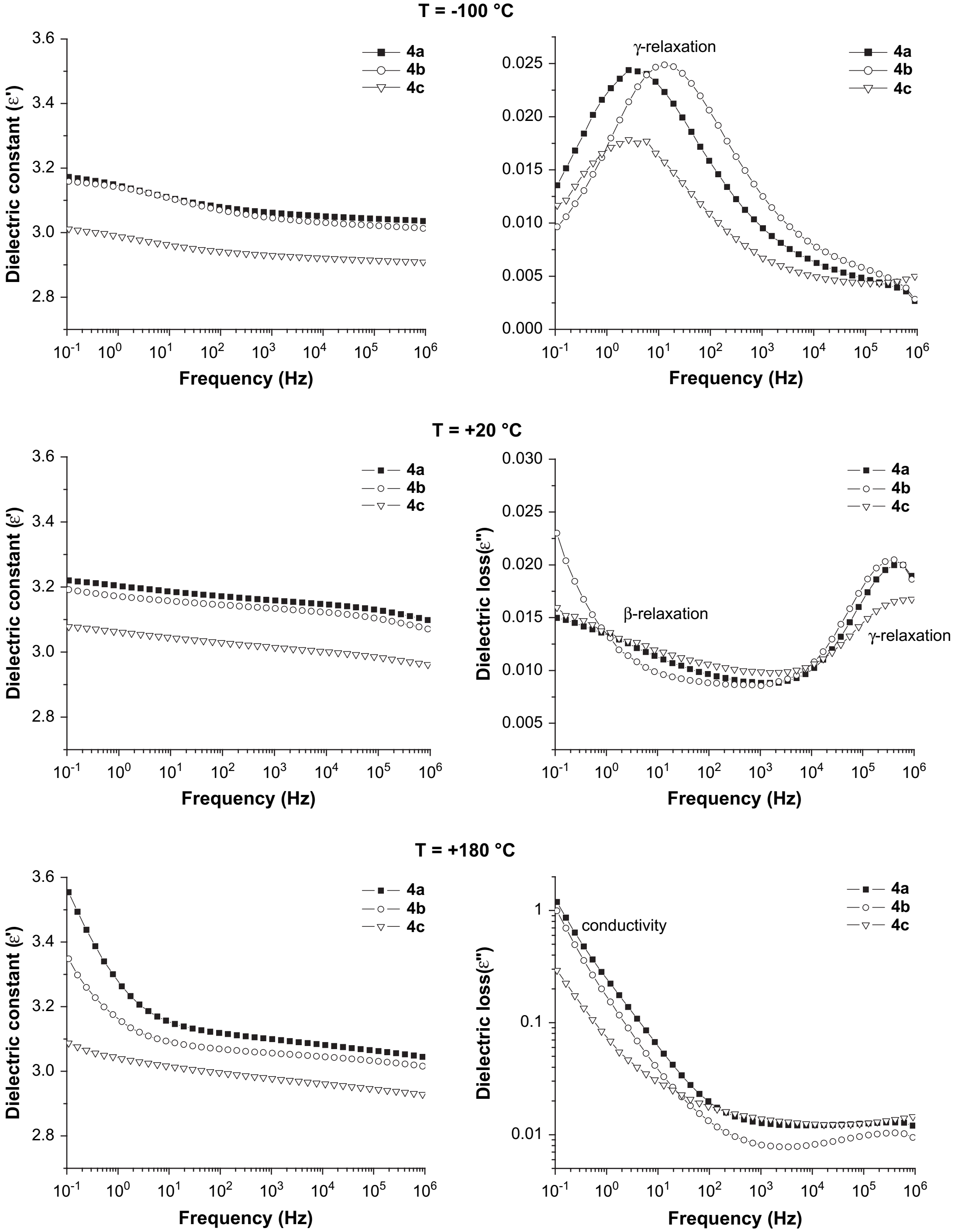


Fig. 7. Dependences of dielectric constant (ε') and dielectric loss (ε'') versus frequency at different temperatures, for polymers **4a–c**.

Table 5
Dielectric constant at selected frequency, at 20 °C, and activation energies of relaxation phenomena calculated from $\varepsilon''(f)$ dependencies, for polymers **4a–c**

Polymer	Dielectric constant at				E_a of γ relaxation [kJ/mol]	E_a of β relaxation [kJ/mol]
	1 Hz	100 Hz	10 kHz	1 MHz		
4a	3.20	3.17	3.15	3.10	42 ± 2	115 ± 10
4b	3.17	3.14	3.12	3.07	39 ± 2	97 ± 7
4c	3.06	3.02	2.98	2.93	47 ± 1	80 ± 15

samples as well as is necessary for calculation of activation energy. Relaxation times (τ) of the secondary relaxation processes at various temperatures have been determined from maxima position of ε'' at frequency scale. The activation plots are shown in Fig. 9. In Table 5 the activation energies of the β and γ relaxation processes calculated on the basis of these diagrams are presented. Because the β relaxation maxima are very weak it is very difficult to determine their exact position and the error in calculation of the activation energy of this relaxation can be in fact bigger that than given in the

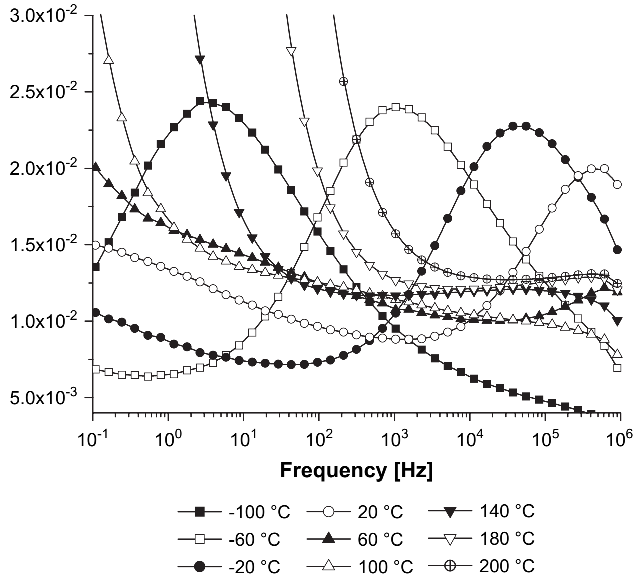


Fig. 8. Dependence of dielectric loss (ε'') versus frequency, at different temperatures, for polymer **4a**.

table. The activation energy for the β relaxation of polymer **4a** containing phthalide groups was higher (115 kJ/mol) than that of polymers **4b** and **4c** containing additional isopropylidene or hexafluoroisopropylidene units coming from the bisphenol monomers (97 kJ/mol and 80 kJ/mol, respectively). But if it takes into account the error in the activation energy calculation, the differences are not so high. The origin of this relaxation is not clear but the most probably is associated with phenyl ring motions. The activation energy values for the γ relaxation of polymers **4a**–**c** were in the range of 39–47 kJ/mol. The closed values of the activation energy for the γ relaxations suggest a common molecular origin. The similar activation energy values of β and γ relaxations were reported for the other heterocyclic polyethers such as poly(phenylquinoxaline-1,3,4-oxadiazole-ether)s or partially aliphatic polyimide copolymers [33,35].

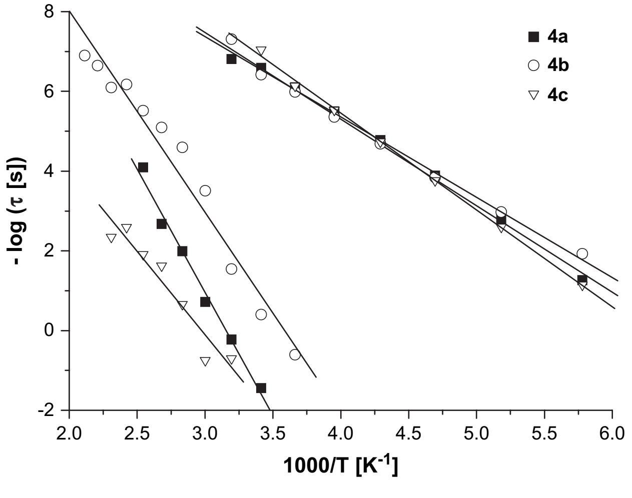


Fig. 9. Activation map for polymers **4a**–**c**.

4. Conclusions

Copoly(1,3,4-oxadiazole-ether)s containing phthalide groups were synthesized. Due to the presence of bulky phthalide groups the polymers were soluble in organic solvents thus being appropriate for processing into transparent films from solutions. The polymers had good thermal stability and high glass transition temperature. The initial decomposition temperature and glass transition temperature depended on the aromatic bisphenol structure used as co-monomer for the synthesis of the polymers. At low and moderate temperature the polymer films studied by dielectric spectroscopy showed two secondary relaxation processes connected with local movements of polymer chains. At moderate temperature the dielectric constant and dielectric loss exhibited low values in the interval of measured frequency, which makes the polymers potential candidates for future high-performance applications in microelectronics or in related fields.

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